

# Antiferro-quadrupole state of orbital-degenerate Kondo lattice model with $f^2$ configuration

Hiroaki ONISHI<sup>1,2</sup> and Takashi HOTTA<sup>1</sup>

<sup>1</sup>Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

<sup>2</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.

(Received October 8, 2007)

To clarify a key role of  $f$  orbitals in the emergence of antiferro-quadrupole structure in  $\text{PrPb}_3$ , we investigate the ground-state property of an orbital-degenerate Kondo lattice model by numerical diagonalization techniques. In  $\text{PrPb}_3$ ,  $\text{Pr}^{3+}$  has a  $4f^2$  configuration and the crystalline-electric-field ground state is a non-Kramers doublet  $\Gamma_3$ . In a  $j$ - $j$  coupling scheme, the  $\Gamma_3$  state is described by two local singlets, each of which consists of two  $f$  electrons with one in  $\Gamma_7$  and another in  $\Gamma_8$  orbitals. Since in a cubic structure,  $\Gamma_7$  has localized nature, while  $\Gamma_8$  orbitals are rather itinerant, we propose the orbital-degenerate Kondo lattice model for an effective Hamiltonian of  $\text{PrPb}_3$ . We show that an antiferro-orbital state is favored by the so-called double-exchange mechanism which is characteristic of multi-orbital systems.

KEYWORDS:  $\text{PrPb}_3$ , antiferro-quadrupole state,  $j$ - $j$  coupling scheme

It is currently one of the central issues in the research field of condensed-matter physics to unveil novel magnetic phases of strongly correlated electron systems with active orbital degrees of freedom. It has been a common understanding that competition and interplay among spin, charge, and orbital degrees of freedom cause diverse ordering phenomena involving multiple degrees of freedom, as frequently observed in  $d$ - and  $f$ -electron systems.<sup>1,2)</sup> In the case of  $f$ -electron systems, spin and orbital are tightly coupled with each other due to the strong intra-atomic spin-orbit interaction. To describe such a complex spin-orbital state, the  $f$ -electron state is usually classified in terms of multipole degrees of freedom.

A rare-earth compound  $\text{PrPb}_3$  with a simple  $\text{AuCu}_3$ -type cubic structure has attracted great interest as a typical material that exhibits antiferro-quadrupolar (AFQ) ordering. In fact, this compound undergoes a second-order transition at 0.4 K,<sup>3)</sup> which has been confirmed to be a non-magnetic but an AFQ transition.<sup>4,5)</sup> In  $\text{PrPb}_3$ ,  $\text{Pr}^{3+}$  has a  $4f^2$  configuration, and the crystalline-electric-field (CEF) ground state is a non-magnetic non-Kramers doublet  $\Gamma_3$  with a magnetic triplet  $\Gamma_4$  lying 19 K above the ground state.<sup>6,7)</sup> The  $\Gamma_3$  state carries  $O_2^0$  and  $O_2^2$  quadrupole moments. Thus, the low-temperature property is governed by quadrupole degrees of freedom.

Regarding the  $H$ - $T$  phase diagram of  $\text{PrPb}_3$ , the so-called reentrant phase diagram has been obtained, in which the transition temperature goes up with increasing the field but turns to decrease and the ordered phase closes at a low field.<sup>7)</sup> This reentrant behavior has been well reproduced phenomenologically based on a mean-field theory assuming a simple two-sublattice ordered structure.<sup>7)</sup> However, recent neutron diffraction measurements have revealed that the quadrupole ordered structure is modulated in space, instead of a simple two-sublattice structure.<sup>8)</sup> In principle, such a long-period ordered structure could emerge because of significant long-range quadrupole interactions, although the origin of the long-range interactions is not clear.

So far, there have been no theoretical efforts to understand AFQ structure of  $\text{PrPb}_3$  from a microscopic viewpoint. In this paper, we propose an orbital-degenerate Kondo lattice model, which is obtained on the basis of a  $j$ - $j$  coupling scheme, as an effective model for  $\text{PrPb}_3$ . We investigate the ground-state

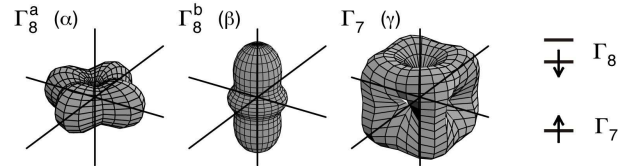


Fig. 1. Schematic view of  $\Gamma_8$  and  $\Gamma_7$  orbitals.

property of the model by using exact-diagonalization techniques. It is found that an antiferro-orbital state emerges due to the so-called double-exchange mechanism which is in general relevant to multi-orbital systems.

First we explain the construction of an effective model for  $\text{PrPb}_3$ . In the  $j$ - $j$  coupling scheme, we first include the strong spin-orbit interaction, and we accommodate  $f$  electrons in the lower sextet with the total angular momentum  $j=5/2$ . Under the cubic CEF effect, the sextet is split into a  $\Gamma_7$  doublet and a  $\Gamma_8$  quartet. To distinguish two Kramers doublets in the  $\Gamma_8$  quartet, it is useful to introduce two orbitals, while spin is also introduced to represent two states in each Kramers doublet. Note that the  $\Gamma_7$  doublet gives another orbital. The schematic views of  $\Gamma_8$  and  $\Gamma_7$  orbitals are depicted in Fig. 1. Since we accommodate  $f$  electrons in the level scheme of the one  $f$ -electron state, we refer to the level scheme of  $\text{CePb}_3$ , which is a  $4f^1$  compound with the same lattice structure with that of  $\text{PrPb}_3$ . In  $\text{CePb}_3$ , it has been found that  $\Gamma_7$  is the ground state and  $\Gamma_8$  is the excited state.<sup>9)</sup> Thus, for  $\text{PrPb}_3$ , we accommodate two  $f$  electrons in this level scheme.

In  $\text{PrPb}_3$ , the CEF ground state is the non-Kramers doublet  $\Gamma_3$ . In the  $j$ - $j$  coupling scheme, the  $\Gamma_3$  state is described by two local singlets, each of which is composed of two electrons with one in  $\Gamma_7$  and another in  $\Gamma_8$  orbitals. Here we note that  $\Gamma_8$  orbitals carry quadrupole degrees of freedom. Taking account of the formation of local singlets, an antiferromagnetic (AFM) coupling should be effective between electrons in  $\Gamma_7$  and  $\Gamma_8$  orbitals, although the Hund's rule coupling causes a ferromagnetic (FM) coupling. Thus, here we introduce the AFM coupling as an effective interaction to involve a high-order CEF effect  $B_6^0$  which can not be included in the  $j=5/2$  Hilbert space in the  $j$ - $j$  coupling scheme.

Concerning the itinerancy and localized nature of orbitals, we consider an  $f$ -electron hopping through the sigma bond. In a cubic structure, due to the spatially anisotropic shape of orbital,  $\Gamma_7$  orbital is localized, while  $\Gamma_8^b$  orbital is itinerant in the  $xy$  plane and  $\Gamma_8^a$  orbital is itinerant in all three directions. Thus, to consider an effective model, we assume that electron in  $\Gamma_7$  orbital is localized, leading to a localized spin. Note that  $\Gamma_8$  electron is itinerant and couples with localized  $\Gamma_7$  spin due to the effective AFM interaction, which can be regarded as an analog of the Kondo coupling.

Taking into account these situations, we obtain an orbital-degenerate Kondo lattice model as an effective Hamiltonian for  $\text{PrPb}_3$ , given by

$$\begin{aligned}
 H = & \sum_{\langle i,j \rangle, \tau, \tau' \sigma} t_{\tau\tau'}^{i-j} f_{i\tau\sigma}^\dagger f_{j\tau'\sigma} + J_K \sum_i \mathbf{S}_{i\Gamma_7} \cdot \mathbf{S}_{i\Gamma_8} \\
 & + U \sum_{i,\tau} \rho_{i\tau\uparrow} \rho_{i\tau\downarrow} + U' \sum_i \rho_{i\alpha} \rho_{i\beta} \\
 & + J \sum_{i,\sigma,\sigma',\tau \neq \tau'} f_{i\tau\sigma}^\dagger f_{i\tau'\sigma'}^\dagger f_{i\tau\sigma'} f_{i\tau'\sigma} \\
 & + J' \sum_{i,\sigma \neq \sigma', \tau \neq \tau'} f_{i\tau\sigma}^\dagger f_{i\tau'\sigma'}^\dagger f_{i\tau'\sigma'} f_{i\tau\sigma} \quad (1)
 \end{aligned}$$

where  $f_{i\tau\sigma}$  is the annihilation operator for  $\Gamma_8$  electron with spin  $\sigma (= \uparrow, \downarrow)$  in orbital  $\tau (= \alpha, \beta)$  at site  $i$ ,  $\rho_{i\tau\sigma} = f_{i\tau\sigma}^\dagger f_{i\tau\sigma}$ ,  $\rho_{i\tau} = \sum_\sigma \rho_{i\tau\sigma}$ ,  $\mathbf{S}_{i\Gamma_8} = (1/2) \sum_{\sigma\sigma'} f_{i\tau\sigma}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} f_{i\tau\sigma'}$ , where  $\boldsymbol{\sigma}_{\sigma\sigma'}$  are Pauli matrices, and  $\mathbf{S}_{i\Gamma_7}$  is the spin-1/2 operator for  $\Gamma_7$  spin. The summation of  $\langle i,j \rangle$  is taken for nearest neighbor sites in the cubic lattice. The hopping amplitudes are evaluated from the overlap integral between  $f$ -orbital wavefunctions in adjacent sites, which are given by  $t_{\alpha\beta}^x = t_{\beta\alpha}^x = -\sqrt{3}t/4$ ,  $t_{\beta\beta}^x = t/4$  for the  $x$  direction,  $t_{\alpha\alpha}^y = t_{\beta\beta}^y = \sqrt{3}t/4$ ,  $t_{\beta\beta}^y = -t/4$  for the  $y$  direction, and  $t_{\beta\beta}^z = t$ ,  $t_{\alpha\alpha}^z = t_{\beta\beta}^z = t_{\beta\alpha}^z = 0$  for the  $z$  direction, where  $t = (3/7)(ff\sigma)$ . Hereafter,  $t$  is taken as the energy unit. In the second term,  $J_K$  is the Kondo coupling between  $\Gamma_7$  spin and  $\Gamma_8$  electron. The rest terms are interactions among  $\Gamma_8$  electrons:  $U$ ,  $U'$ ,  $J$ , and  $J'$  denote intra-orbital, inter-orbital, exchange, and pair-hopping interactions, respectively. Note that the relation  $U = U' + J + J'$  holds, which originates from the rotational invariance in the orbital space, and  $J = J'$  is assumed.<sup>2)</sup>

We analyze the model (1) by numerical diagonalization. Since the size of the Hilbert space becomes so large as  $32^N$  due to orbital degree of freedom, where  $N$  is the number of sites, it is rather difficult to enlarge the system size. However, the method is advantageous to grasp the ground-state property, such as orbital structure, in an unbiased manner. In the present work, first we study a  $2 \times 2$  square four-site system in the  $xy$  plane. Then, taking account of the characteristics grasped within the four-site system, we proceed to a  $2 \times 2 \times 2$  cubic eight-site system. In this paper, we set  $U'/W = 2$ , where  $W$  is the band width, and investigate the dependence on  $J_K$  and  $J$ . Note that the band width is  $W = 4$  for the square system and  $W = 6$  for the cubic system.

First, we show the results for the four-site system. The main result is summarized in Fig. 2(a), which is the ground-state phase diagram in the  $(J_K, J)$  plane. There three types of competing spin-orbital configurations are observed. When  $J_K$  and  $J$  are small, we find a ferro-orbital (FO) state with an AFM

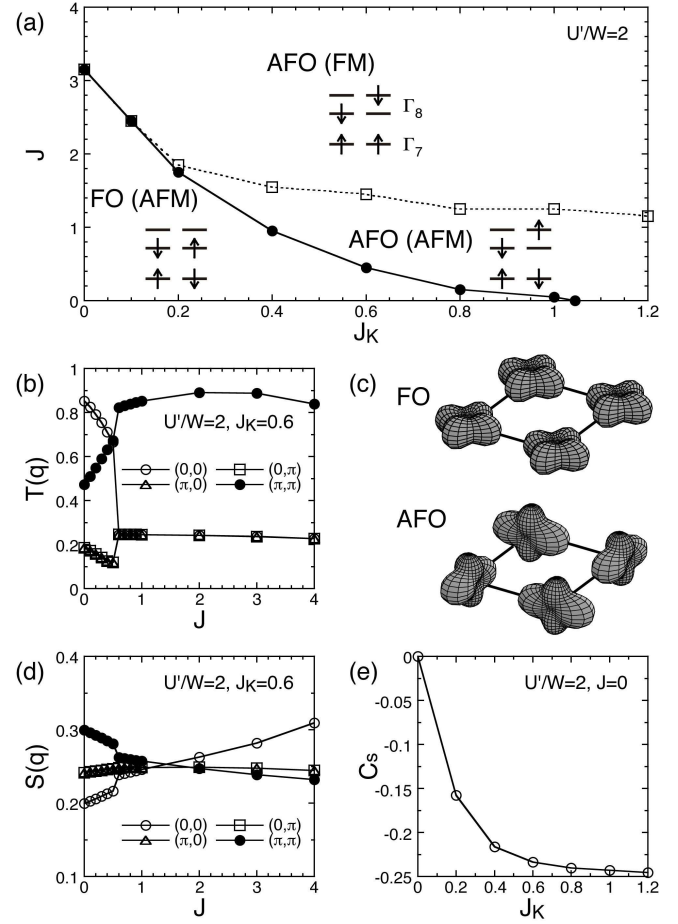


Fig. 2. Four-site results. (a) Ground-state phase diagram in the  $(J_K, J)$  plane. Inset denotes schematic view of electron configuration in each phase. (b)  $T(\mathbf{q})$  as a function of  $J$  at  $J_K = 0.6$ . (c) FO and AFO structures. (d)  $S(\mathbf{q})$  as a function of  $J$  at  $J_K = 0.6$ . (e)  $C_s$  as a function of  $J_K$  at  $J = 0$ . Note that  $C_s(i)$  takes the equivalent value at every site due to the translational symmetry.

configuration in each of  $\Gamma_7$  and  $\Gamma_8$  orbitals, while spins in  $\Gamma_7$  and  $\Gamma_8$  orbitals are antiparallel at each site due to  $J_K$ . With increasing  $J$ , an antiferro-orbital (AFO) state occurs, and the spin state turns to be FM at a larger  $J$  than the transition point from FO to AFO. It should be noted that even though the spin state is characterized by AFM or FM in each of  $\Gamma_7$  and  $\Gamma_8$  orbitals, a local singlet is formed due to  $J_K$  and the ground state is totally non-magnetic.

Let us here discuss the orbital state. In order to determine the orbital structure, it is useful to introduce new operators for  $\xi$  and  $\eta$  orbitals, which are given by linear combinations of the original operators, such as

$$\begin{aligned}
 \tilde{f}_{i\xi\sigma} &= \cos(\theta_i/2) f_{i\beta\sigma} + \sin(\theta_i/2) f_{i\alpha\sigma}, \\
 \tilde{f}_{i\eta\sigma} &= -\sin(\theta_i/2) f_{i\beta\sigma} + \cos(\theta_i/2) f_{i\alpha\sigma}, \quad (2)
 \end{aligned}$$

where  $\theta_i$  characterizes the orbital shape at each site. The optimal  $\{\theta_i\}$  is determined so as to maximize the orbital structure factor, defined by

$$T(\mathbf{q}) = \sum_{\mathbf{j}, \mathbf{k}} \langle \tilde{T}_{\mathbf{j}}^z \tilde{T}_{\mathbf{k}}^z \rangle e^{i\mathbf{q} \cdot (\mathbf{j} - \mathbf{k})} / N, \quad (3)$$

where  $\tilde{T}_i^z = \sum_\sigma (\tilde{f}_{i\xi\sigma}^\dagger \tilde{f}_{i\xi\sigma} - \tilde{f}_{i\eta\sigma}^\dagger \tilde{f}_{i\eta\sigma}) / 2$  and  $\langle \dots \rangle$  denotes the

expectation value. In Fig. 2(b), we show  $T(\mathbf{q})$  as a function of  $J$  at  $J_K=0.6$  with  $\theta_1=\theta$ . For small  $J$ , the dominant component is  $T(0,0)$  with  $\theta=\pi$ , indicating FO state. In the FO state of the present square system in the  $xy$  plane,  $\Gamma_8^a$  orbitals are favorably occupied to gain kinetic energy, since  $\Gamma_8^a$  orbital extends to adjacent sites, as shown in Fig. 2(c). With increasing  $J$ , the dominant component changes to  $T(\pi, \pi)$  with  $\theta=\pi/2$ , indicating AFO state in Fig. 2(c). We note that the present square lattice structure is reflected in the orbital shape. In this context, it is crucial to proceed to the eight-site system to discuss the orbital structure in the cubic lattice.

Concerning the spin state, we measure the spin structure factor of  $\Gamma_8$  electrons, defined by

$$S(\mathbf{q}) = \sum_{\mathbf{j}, \mathbf{k}} \langle S_{\mathbf{j}\Gamma_8}^z S_{\mathbf{k}\Gamma_8}^z \rangle e^{i\mathbf{q} \cdot (\mathbf{j} - \mathbf{k})} / N. \quad (4)$$

As shown in Fig. 2(d), with increasing  $J$ ,  $S(0,0)$  is increased, while  $S(\pi, \pi)$  is reduced, so that the dominant spin correlation changes from AFM to FM. Here we note that the motion of  $\Gamma_8$  electrons leads to a FM spin arrangement. Namely, the double-exchange mechanism is effective, which is characteristics of multi-orbital systems.

We also measure the on-site spin correlation, defined by

$$C_s(\mathbf{i}) = \langle S_{\mathbf{i}\Gamma_7}^z S_{\mathbf{i}\Gamma_8}^z \rangle. \quad (5)$$

In Fig. 2(e), the  $J_K$  dependence of  $C_s$  at  $J=0$  is shown. It is obvious that  $C_s=0$  at  $J_K=0$ , since there is no correlation between  $\Gamma_7$  spin and  $\Gamma_8$  electron. With increasing  $J_K$ ,  $C_s$  decreases and gradually approaches  $-1/4$ , indicating the stabilization of the local singlet. It is found that even when  $J$  is increased,  $C_s$  keeps a value near  $-1/4$  (not shown), indicating the robust formation of the local singlet. Here it is worth noting that as  $J_K$  increases and the local singlet is stabilized, the AFO phase tends to extend to the region of small  $J$ , as shown in Fig. 2(a). Namely, the double-exchange mechanism becomes significant due to  $J_K$ .

Now we move on to the results for the eight-site system. In Fig. 3(a), we show the  $\theta$  dependence of  $T(\mathbf{q})$  at  $J_K=1$  and  $J=0$ . We find that  $T(\pi, \pi, \pi)$  is dominant, indicating AFO state. Concerning the orbital shape, it is observed that the magnitude of  $T(\pi, \pi, \pi)$  does not depend on  $\theta$ . We can not determine the actual orbital shape, but the AFO structure with any  $\theta$  is possible to realize. The AFO structure with  $\theta=0$  is shown in Fig. 3(b). As for the spin state,  $S(\pi, \pi, \pi)$  is found to be dominant. We note that the present parameter set ( $J_K=1$  and  $J=0$ ) is corresponding to the FO phase in the four-site system, as shown in Fig. 2(a). It is naively expected that the AFO phase extends to a broad area in the phase diagram even when we consider the cubic lattice. However, at  $J_K=1$  and  $J=4$ ,  $T(\mathbf{q})$  has dominant components  $T(\pi, \pi, 0)$  with  $\theta=\pi/2$ ,  $T(\pi, 0, \pi)$  with  $\theta=5\pi/6$ , and  $T(0, \pi, \pi)$  with  $\theta=\pi/6$ , as shown in Fig. 3(c), while  $S(0, 0, 0)$  is dominant. The  $(\pi, \pi, 0)$  orbital structure is depicted in Fig. 3(d). When  $J$  is further increased, the orbital structure is considered to turn to be AFO due to the double-exchange mechanism, suggesting a rich phase diagram including competing orbital states.

Finally, we briefly discuss possible relevance of the present results to the AFQ structure of  $\text{PrPb}_3$ . We have shown that for a one-dimensional  $j$ - $j$  coupling model with an  $f^1$  configuration,<sup>10)</sup> an incommensurate orbital state appears due to

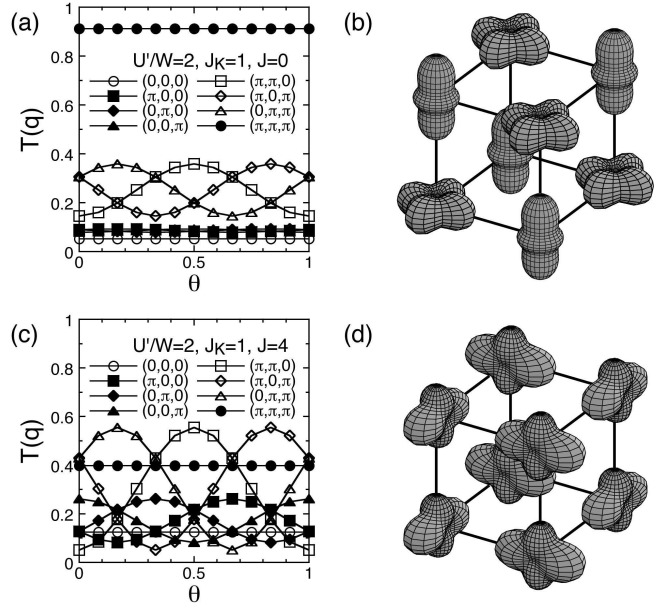


Fig. 3. Eight-site results. (a)  $T(\mathbf{q})$  as a function of  $\theta$  and (b) orbital structure at  $J_K=1$  and  $J=0$ . (c)  $T(\mathbf{q})$  as a function of  $\theta$  and (d) orbital structure at  $J_K=1$  and  $J=4$ .

the competition between itinerant and localized orbitals. By analogy, we expect that the competition among plural orbital states with different nature could cause a modulated orbital structure as observed in  $\text{PrPb}_3$ .

In summary, we have investigated the ground-state property of the orbital-degenerate Kondo lattice model to understand the quadrupole structure in  $\text{PrPb}_3$  from a microscopic viewpoint. We have observed several types of competing spin-orbital states. In particular, it has been emphasized that the AFO state emerges due to the double-exchange mechanism.

The authors have been supported by a Grant-in-Aid for Scientific Research in Priority Area “Skutterudites” under the contract No. 18027016 from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. T.H. has been also supported by a Grant-in-Aid for Scientific Research (C) under the contract No. 18540361 from Japan Society for the Promotion of Science.

- 1) M. Imada, A. Fujimori and Y. Tokura: Rev. Mod. Phys. **70** (1998) 1039.
- 2) T. Hotta: Rep. Prog. Phys. **69** (2006) 2061.
- 3) E. Bucher, K. Andres, A. C. Gossard and J. P. Maita: J. Low Temp. Phys. **2** (1972) 322.
- 4) P. Morin, D. Schmitt and E. du Tremolet de Lacheisserie: J. Magn. Magn. Mater. **30** (1982) 257.
- 5) M. Niksch, W. Assmus, B. Lüthi, H.R. Ott and J.K. Kjems: Helv. Phys. Acta **55** (1982) 688.
- 6) W. Groß, K. Knorr, A.P. Murani and K.H.J. Buschow: Z. Physik B **37** (1980) 123.
- 7) T. Tayama, T. Sakakibara, K. Kitami, M. Yokoyama, K. Tenya, H. Amitsuka, D. Aoki, Y. Ōnuki and Z. Kletowski: J. Phys. Soc. Jpn. **70** (2001) 248.
- 8) T. Onimaru, T. Sakakibara, N. Aso, H. Yoshizawa, H.S. Suzuki and T. Takeuchi: Phys. Rev. Lett. **94** (2005) 197201.
- 9) D. Nikl, I. Kouroudis, W. Assmus, B. Lüthi, G. Bruls and U. Welp: Phys. Rev. B **35** (1987) 6864.
- 10) H. Onishi and T. Hotta: Proc. 5th Int. Symp. ASR-WYP-2005: Advances in the Physics and Chemistry of Actinide Compounds, J. Phys. Soc. Jpn. **75** (2006) Suppl., p. 266.